

**Surface Tensions and Thermal Conductivities of Aqueous LiBr-Based Solutions
Containing n-Octanol and 2-Ethyl-1-Hexanol: Application to Absorption Heat
Pump¹**

S. B. Park², J. W. Lee², and H. Lee^{2,3}

¹ Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25-30, 2000, Boulder, Colorado, U.S.A.

² Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Teajon, South Korea.

³ To whom correspondence should be addressed.

ABSTRACT

Surface tensions and thermal conductivities were measured for LiBr + 1,3-propanediol + water and LiBr + LiI + 1,3-propanediol + water. These two mixtures were chosen as one of the potential candidates of working fluids for absorption heat pump. Surface tensions and thermal conductivities were measured by the capillary rise method equipped with cathetometer and the transient hot wire method with coated tantalum wire, respectively. The measured surface tension and thermal conductivity data were well correlated as a simple polynomial function expressed with temperature and absorbent concentration. In addition, the surface tensions of LiBr + 1,3-propanediol + water containing a small amount of alcohol-based surfactants, n-octanol and 2-ethyl-1-hexanol, were also measured at 298.15 K by the ring method. With increasing the surfactant concentration up to about 500 ppm, the mixture surface tensions gradually decreased.

KEY WORDS: absorption heat pump; capillary rise method; surface tension; thermal conductivity; transient hot wire method.

INTRODUCTION

The aqueous electrolyte solutions with organics are frequently asserted in the industrial processes. Many research areas such as interfacial phenomena, colloidal system, gas absorption and absorption heat pump require the reliable data of surface tension and thermal conductivity of aqueous electrolyte solutions. The highly concentrated aqueous LiBr-based solutions have been commonly used as working fluids for absorption heat pump. In this connection, many studies on surface tension related to absorption heat pump have been mainly restricted to the aqueous LiBr solutions [1,2]. In our previous studies, LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5 by mass) and LiBr + LiI + 1,3-propanediol + water (LiBr/LiI = 4 by mole and (LiBr + LiI)/1,3-propanediol = 4 by mass) mixtures were suggested as a possible candidate for air-cooled absorption chillers [3,4]. In this study, the surface tensions of these two mixtures were measured by capillary rise method in order to provide the basic information of the new working fluids. In particular, the decrease of surface tension by alcoholic additives greatly influences the heat/mass transfer enhancement of absorption heat pump. To examine this additive effect the surface tensions of LiBr + 1,3-propanediol + water with n-octanol and 2-ethyl-1-hexanol at 298.15 K were measured by ring method.

Besides surface tension the optimum design of the individual units of absorption heat pump including heat transfer analysis requires the reliable thermal conductivity data at the operating conditions. Recently, the transient hot wire method [5,6,7] has been widely used to measure thermal conductivity for gas and liquid mixtures. This method comprises many advantages such as exclusion of the convection error, fast measurement, high accuracy and better reproducibility compared with the steady state

method. In order to apply the transient hot wire method to electrolyte solutions a proper insulation of metal wire is needed. In this study, a tantalum wire coated by anodization was used to overcome problems caused by the bare wire. The measured surface tension and thermal conductivity data were well correlated with a simple polynomial function expressed with temperature and concentration.

2. EXPERIMENTALS

2.1. Materials

Lithium bromide (+99.5 %), lithium iodide (+99.5 %), and 1,3-propanediol (+98 %) manufactured by Sigma-Aldrich chemical company were used without further purification. The water used in making all solutions was triple-distilled.

2.2. Surface tension

The apparatus for the capillary rise method consists of the water bath, bath circulator, capillary tube, thermometer, and cathetometer. The temperature of a capillary tube was controlled by the bath circulator (JEIO tech. RBC-20) within ± 0.1 K. The temperature of fluid in the capillary tube was measured by the thermometer with an accuracy of ± 0.1 K. The height of the liquid rise in the capillary tube was measured by the cathetometer (N.O.W. NCM 30) with an accuracy of 10^{-5} m. Determination of the capillary radius was carried out by using benzene as a standard chemical basis. During the experiment, the height difference between capillary and outer tube meniscus was measured with using the cathetometer. The height difference was measured at least five times for each data point with a reproducibility of $\pm 2 \cdot 10^{-4}$ m. The surface tension can be then calculated from a simple equation including the radius of capillary, height difference between two meniscus, and density of a sample.

The surface tensions of electrolyte solutions containing additives were measured by a commercially available dynamic contact angle analyzer (DCA314, Cahn Corp.) using the ring method. Since the experimental apparatus and procedure by ring method is elsewhere available [1], the detailed description was omitted. The temperature of the solution was kept to 298.15 K with an accuracy of ± 0.1 K. The experiments were carried out under the automatic operation controlled by the attached electrical system. The measurements were performed at least three times and the reproducibility was within ± 0.5 %.

2.3. Thermal conductivity

The measurement was performed in an absolute manner with coated tantalum wire. Since the detailed description of the experimental procedure and the reduction of the raw data are available in the literature [5,6,7], only the revised parts of our apparatus are introduced in this paper. The schematic diagram of the experimental apparatus is presented in Fig. 1. The whole apparatus is divided into two major parts of Whetstone bridge and measurement system. The Whetstone Bridge includes two standard resistors of $10\text{ K}\Omega$, a variable resistor, and a coated tantalum wire used as both a heat source and a detector of temperature rise. A tantalum (99.9%) wire with nominal diameter of $25\mu\text{m}$ from E.S.P.I. company was mounted to the cell by spot wedging. The length of the wire was measured by cathetometer with an accuracy of 10^{-5} m. The wire was anodized to form tantalum pentoxide by the method described in the literature [5]. The fluid temperature was measured by a K-type thermocouple penetrated to the cell with an accuracy of ± 0.1 K. The whole cell was placed in the water bath of which the temperature was controlled by an external circulator within ± 0.2 K. The measurement system consists of two digital multimeters (DMM), a function generator, a power

supply, and a personal computer. The DMM (HP3410) equipped with the HP-IB interface was purchased from Hewlett Packard company and connected to the computer in order to receive the offset voltage from the Wheatstone Bridge and the applied power from the power supply. A power supply for the step voltage input and a function generator for the external triggering were manufactured by LG electronics. The offset voltage and the applied power were simultaneously recorded to the computer controlled by visual basic program.

3. RESULTS

3.1. Surface tension

The surface tensions measured by the capillary rise method were calculated from the following simple equation

$$\gamma = \frac{1}{2} \cdot h \cdot r \cdot d \cdot g \quad (1)$$

where γ is the surface tension, h the height difference between capillary and outer tube meniscus, r the capillary radius, d the density of sample, and g the gravitational acceleration. To determine the radius of capillary tube, the calibration was carried out using the known surface tension and density of benzene. The resulting radius of capillary tube was found to be $2.71 \cdot 10^{-4}$ m. To check the reliability of the experimental apparatus and procedures used in this study, the surface tensions of the LiBr + water solution were measured at various temperatures and found to be in good agreement with the literature values [8] as shown in Fig. 2. The maximum deviation was less than 2.0 AAD %, which is acceptable in the measurement of surface tension. The surface tensions of the LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5 by mass) system were measured at the temperature range of 298.15 to 323.15 K and the absorbent

concentration range up to 65 mass %. The experimental results are presented in Fig. 3. As shown in this figure, the surface tension of the ternary system decreased as the temperature increased over the entire absorbent concentration range. The temperature effect on surface tension decreases with increasing the absorbent concentration. The surface tensions of the solutions highly concentrated with absorbents of LiBr + 1,3-propanediol became smaller than those of the diluted solutions, which is the opposite trend quite different from the surface tensions of LiBr + water solution shown in Fig. 2. This might be due to the low surface tension of 1,3-propanediol contained in the solution. The increase of LiBr as well as 1,3-propanediol concentrations made the overall surface tensions of the mixed solutions lower. The experimental surface tension data were correlated with the polynomial equation expressed as follows

$$\sigma = \sum_{i=0}^2 [(A_i + B_i \cdot T + C_i \cdot T^2) \cdot X^i] \quad (2)$$

σ is the surface tension in $\text{mN} \cdot \text{m}^{-1}$, T the temperature in K, and X the mass % of the absorbent, respectively. The resulting coefficients used in equation 2 are listed in Table 1. The overall average absolute deviation (AAD%) was found to be 0.188.

The surface tensions of LiBr + LiI + 1,3-propanediol + water (LiBr/LiI = 4 by mole and (LiBr+LiI)/1,3-propanediol = 4 by mass) were measured up to 53 mass % of absorbent concentration with a temperature range from 298.15 to 323.15 K and shown in Fig. 4. The effect of absorbent concentration and temperature of this mixture appeared to be similar to that of LiBr + 1,3-propanediol + water. The experimental surface tensions of LiBr + LiI + 1,3-propanediol + water were fitted to the following equation.

$$\sigma = \sum_{i=0}^2 [(A_i + B_i \cdot T) \cdot X^i] \quad (3)$$

The resulting regressed coefficients are listed in Table 2. The overall deviation between the experimental results and the calculated values was found to be 0.286 in AAD%.

In addition, the surface tensions of LiBr + 1,3-propanediol + water with n-octanol and 2-ethyl-1-hexanol were measured at 298.15 K by the Dunoy ring method. The used absorbent concentrations of LiBr + 1,3-propanediol, were 54.5 and 67.9 mass %. As shown in Fig. 5 and 6, the addition of n-octanol and 2-ethyl-1-hexanol up to approximately 25 ppm has a little influence on decreasing surface tensions of the solution, but above 25 ppm the surface tensions abruptly decrease. The decreasing rate of surface tension in the absorbent concentration of 67.9 mass % is steeper than that in the absorbent concentration of 54.5 mass % solutions. The critical concentrations of two additives appeared near a few hundreds ppm and above this concentration the surface tension did not decrease furthermore. The critical concentration of n-octanol was higher than that of 2-ethyl-1-hexanol because of the higher solubility of n-octanol than 2-ethyl-1-hexanol in the solution [9].

3.2. Thermal conductivity

To verify the experimental apparatus and procedure, thermal conductivities of the aqueous 15.3 mass % NaCl solution were measured and compared with the literature data of Nagasaka and Nagashima [10]. The reduction of thermal conductivity from the offset voltage and correction of temperature to compensate the deviation from ideal model were carried out by the similar manner given in the literature [5,6,7,10]. The experimental results were in an agreement within ± 1 %. In this work, the total correction for the temperature rise was less than ± 0.7 % and was found to have a negligible effect on thermal conductivity. The measurements of thermal conductivity

were performed for the LiBr + 1,3-propanediol + water and LiBr + LiI + 1,3-propanediol + water solutions with the same absorbent ratios in the temperature range from 285 to 305 K. The concentrations of the absorbents treated in this work are 67.9 mass % for LiBr + 1,3-propanediol + water and 69.9 mass % for LiBr + LiI + 1,3-propanediol + water system. The corresponding density and heat capacity data for the temperature correction were obtained from our previous works [3,4]. The experimental data were listed in Table 3 and graphically presented in Fig. 7. The solution thermal conductivity slightly increased with temperature, which is similar to the trend of the aqueous LiBr solution. Considering the working fluid condition in an absorber of air-cooled absorption chillers, the present thermal conductivity data are expected to give the basic information for the design of absorption system. Each data set was satisfactorily regressed to linear equations of $\lambda = 0.222 + 0.000635T$ for LiBr + 1,3-propanediol + water and $\lambda = 0.215 + 0.000596T$ for LiBr + LiI + 1,3-propanediol + water. λ is the thermal conductivity measured in $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, T the temperature in Kelvins. The deviation between the experimental and calculated values did not exceed 0.4 AAD%.

4. CONCLUSION

Surface tensions of the LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5 by mass) and LiBr + LiI + 1,3-propanediol + water (LiBr/LiI = 4 by mole and (LiBr+LiI)/1,3-propanediol = 4 by mass) system were measured by capillary rise method. The mixture surface tensions decreased with increasing temperature and concentration of the absorbents. The experimental data were successfully regressed by the simple polynomial equations. The effect of an alcoholic surfactant on the surface tension was investigated for LiBr + 1,3-propanediol + water at 298.15 K. The addition

of the surfactant decreased abruptly the solution surface tension particularly in the high absorbent concentration. The thermal conductivities of the same system were measured by the transient hot wire method with a coated tantalum wire at the concentration of which the treated solutions exist in the absorber in an air-cooled absorption chillers. The experimental thermal conductivities increased with temperature and well regressed by a linear equation of temperature.

ACKNOWLEDGMENTS

This work was supported by grant No. 97-2-10-03-01-3 from the Basic Research Program of KOSEF and also partially by the Brain Korea 21 Project.

REFERENCES

1. K. J. Kim, N. S. Berman, and B. D. Wood, *J. Chem. Eng. Data* **39**: 122 (1994).
2. W. Yao, H. Bjurstorm, and F. Setterwall, *J. Chem. Eng. Data* **36**: 96 (1991).
3. Y. Park, J. S. Kim, and H. Lee, *Int. J. Refrig.* **20**: 319 (1997).
4. J. S. Kim and H. Lee, *J. J. Chem. Eng. Data* submitted.
5. A. Alloush, W. B. Gosney, and W. A. Wakeham, *Int. J. Thermophys.* **3**: 225 (1982).
6. M. L. V. Ramires, J. M. N. A. Fareleira, C. A. Nieto de Castro, M. Dix, and W. A. Wakeham, *Int. J. Thermophys.* **14**: 1119 (1993).
7. M. L. V. Ramires, J. C. A. Nieto de Castro, M. N. A. Fareleira, and W. A. Wakeham, *J. Chem. Eng. Data* **39**: 186 (1994).
8. T. Uemura, S. Hasaba, *Tech Rep. Kansai Univ.* **6**: 31 (1964).
9. A. S. Kertes and A. F. M. Barton, in *Solubility Data Series-Alcohols with Water*, Vol 15, Pergamon, press Inc. (Int. Union of Pure and Applied Chem., NewYork, 1984), p. 359.
10. Y. Nagasaka and A. Nagashima, *J. Phys. E.: Sci. Instrum.*, **14**: 1435 (1981).

Table I. The Coefficients Regressed in Equation (2) for the Surface Tension of LiBr +
1,3-Propanediol + Water (LiBr/1,3-Propanediol = 3.5 by Mass)

	Ai	Bi	Ci
i=0	1.337E+02	- 2.485E-01	1.379E-04
i=1	-3.078E+00	1.676E-02	-2.214E-05
i=2	2.853E-02	-1.767E-04	2.628E-07

Table II. The Coefficients Regressed in Equation (3) for the Surface Tension of LiBr + LiI + 1,3-Propanediol + Water (LiBr/LiI = 4 by Mole and (LiBr+LiI)/1,3-Propanediol = 4 by Mass)

	i=0	i=1	i=2
A _i	1.336E+02	-1.459E+02	1.117E+02
B _I	-2.095E-01	4.878E-01	-4.475 E-01

Table III. Thermal Conductivities of LiBr + 1,3-Propanediol + Water (LiBr/1,3-Propanediol = 3.5 by mass) and LiBr + LiI + 1,3-Propanediol + Water (LiBr/LiI = 4 by Mole and (LiBr + LiI)/1,3-Propanediol = 4 by Mass)

Absorbent mass %	Temperature	Thermal conductivity,
X	T(K)	λ (W·m ⁻¹ ·K ⁻¹)
LiBr + 1,3-propanediol + water		
67.9	286.5	0.403
	295.3	0.410
	305.3	0.415
LiBr + LiI + 1,3-propanediol + water		
69.9	285.1	0.385
	297.2	0.391
	303.0	0.396

FIGURE CAPTIONS

Fig. 1. Schematic diagram of the experimental apparatus for thermal conductivity measurement.

Fig. 2. Surface tensions of LiBr + water at 298.15 K against the mass % of LiBr; ●, this work; –, reference [8].

Fig. 3. Surface tensions of LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5 by mass) at various temperature: ●, T = 298.15 K; ○, T = 303.15 K; ▼, T = 308.15 K; ▽, T = 313.15 K; ■, T = 318.15 K; □, T = 323.15 K; –, calculated values.

Fig. 4. Surface tensions of LiBr + LiI + 1,3-propanediol + water (LiBr/LiI = 4 by mole and (LiBr + LiI)/1,3-propanediol = 4 by mass) at various temperature; ●, T = 298.15 K; ○, T = 303.15 K; ▼, T = 308.15 K; ▽, T = 313.15 K; ■, T = 318.15 K; □, T = 323.15 K; –, calculated values.

Fig. 5. Surface tensions of 54.5 mass % LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5 by mass) solution with n-octanol and 2-ethyl-1-hexanol at 298.15 K; ●, 2-ethyl-1-hexanol; ○, n-octanol.

Fig. 6. Surface tensions of 67.9 mass % LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5 by mass) solution with n-octanol and 2-ethyl-1-hexanol at 298.15 K; ●, 2-ethyl-1-hexanol; ○, n-octanol.

Fig. 7. Thermal conductivities of 67.9 mass % LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5 by mass) and 69.9 mass % LiBr + LiI + 1,3-propanediol + water (LiBr/LiI = 4 by mole and (LiBr + LiI)/1,3-propanediol = 4 by mass) against temperature; ●, LiBr + 1,3-propanediol + water; ○, LiBr + LiI + 1,3-propanediol + water.

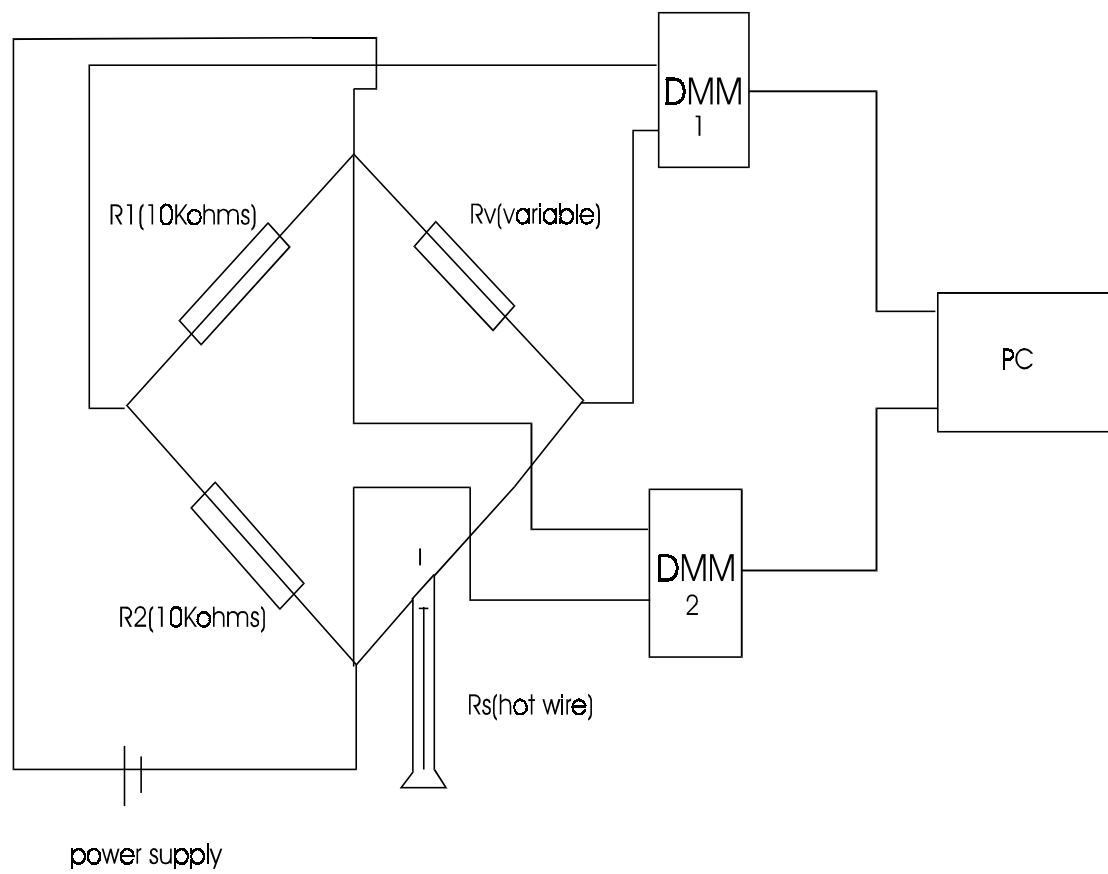


Fig. 1

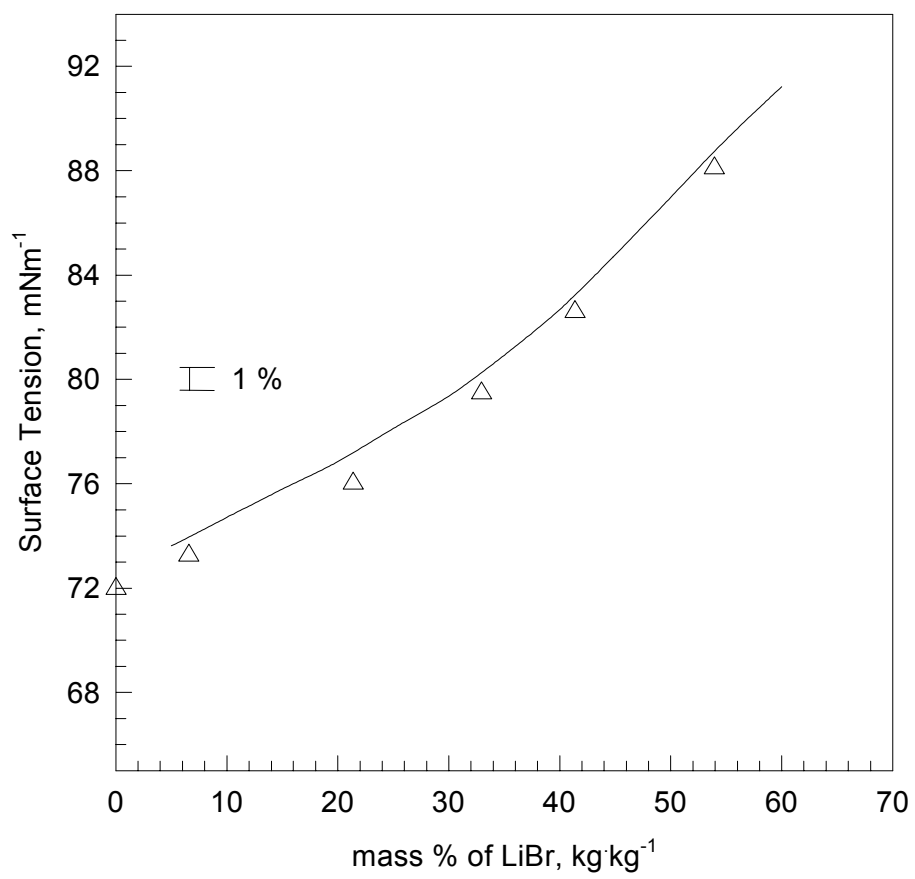


Fig. 2

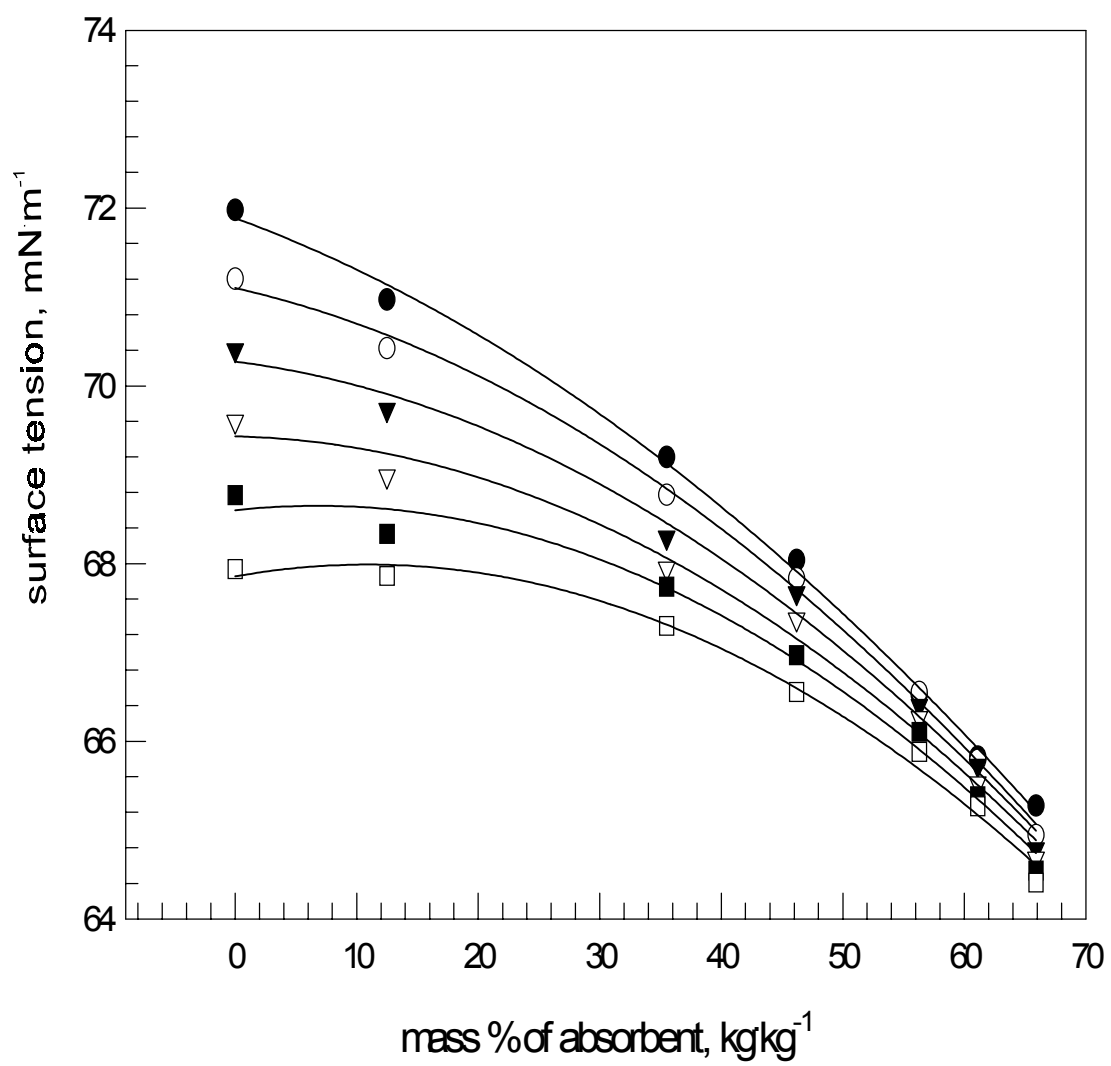


Fig. 3

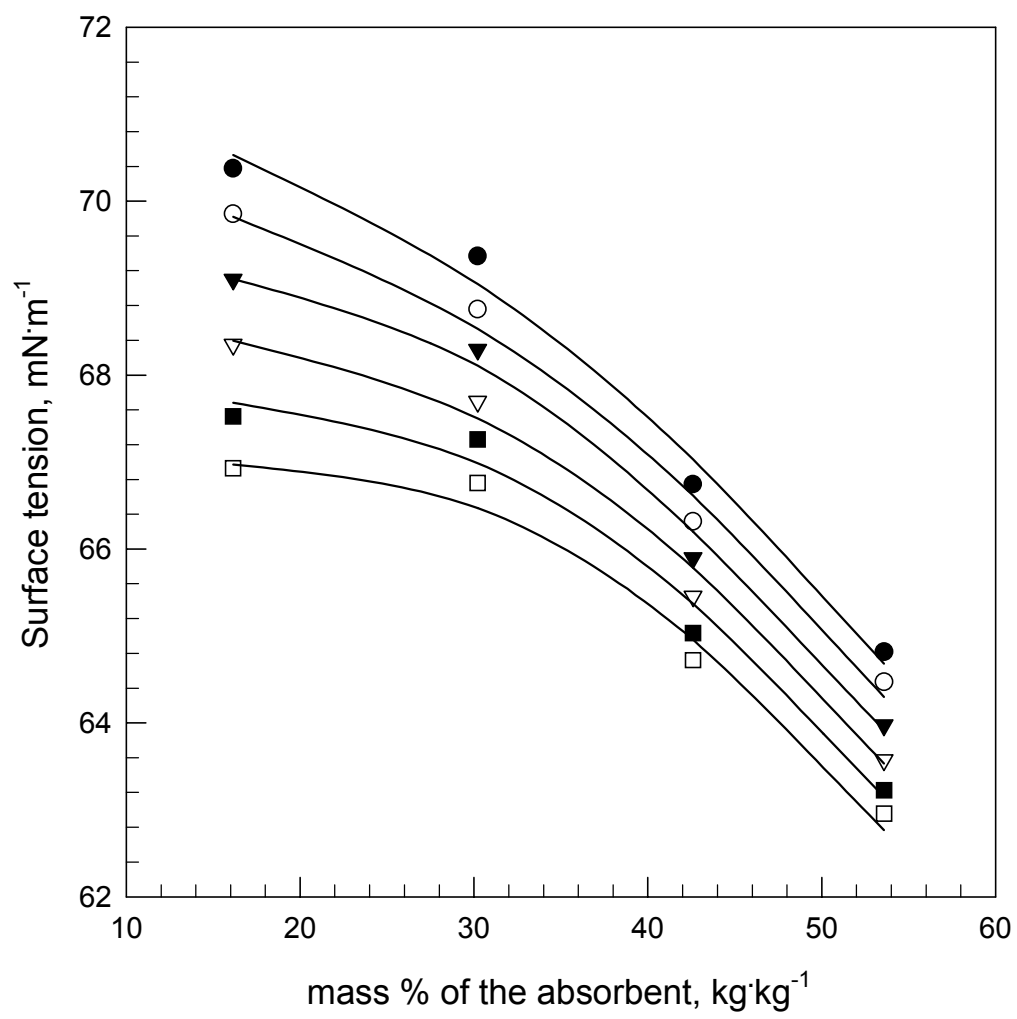


Fig. 4

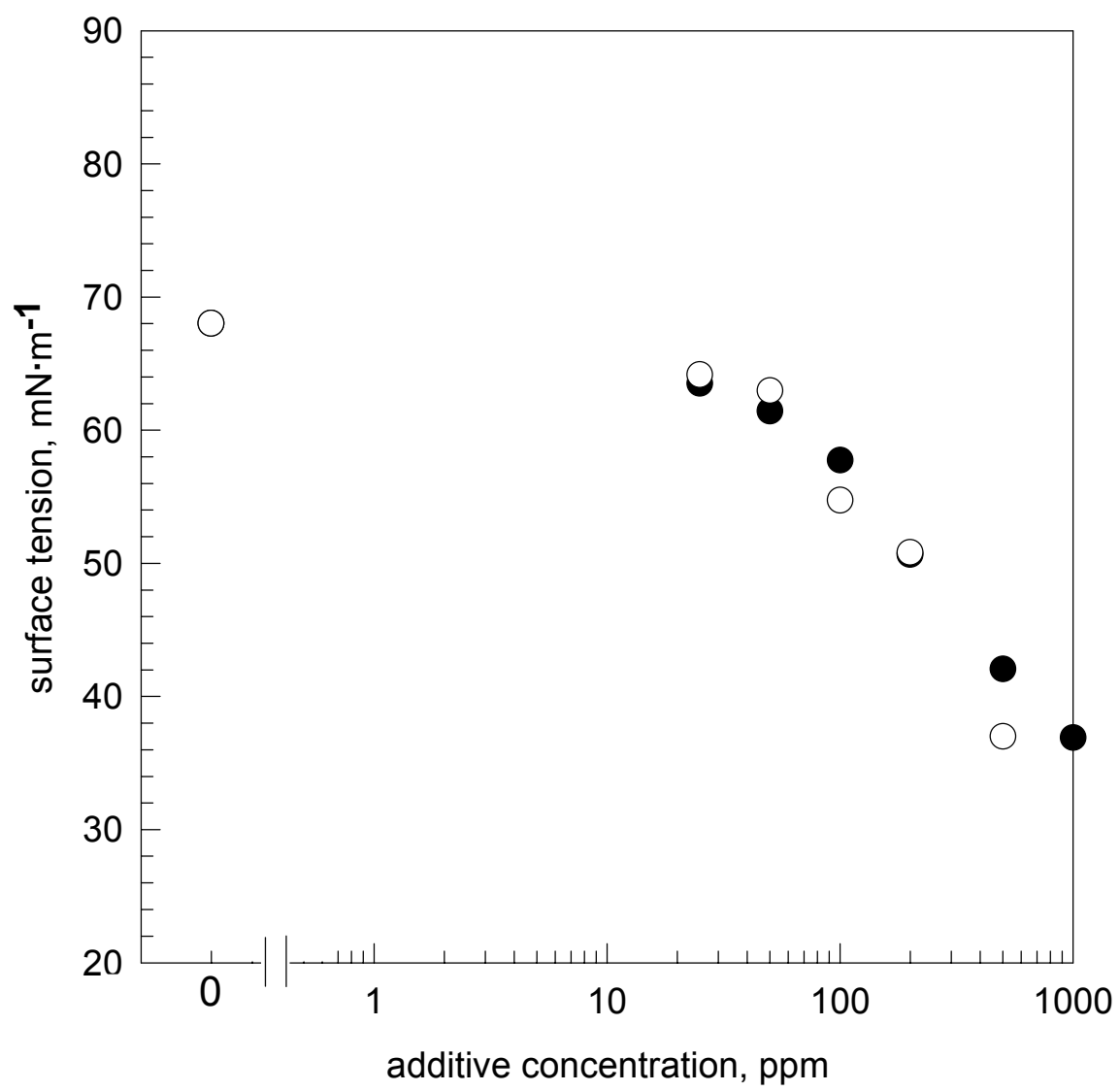


Fig. 5

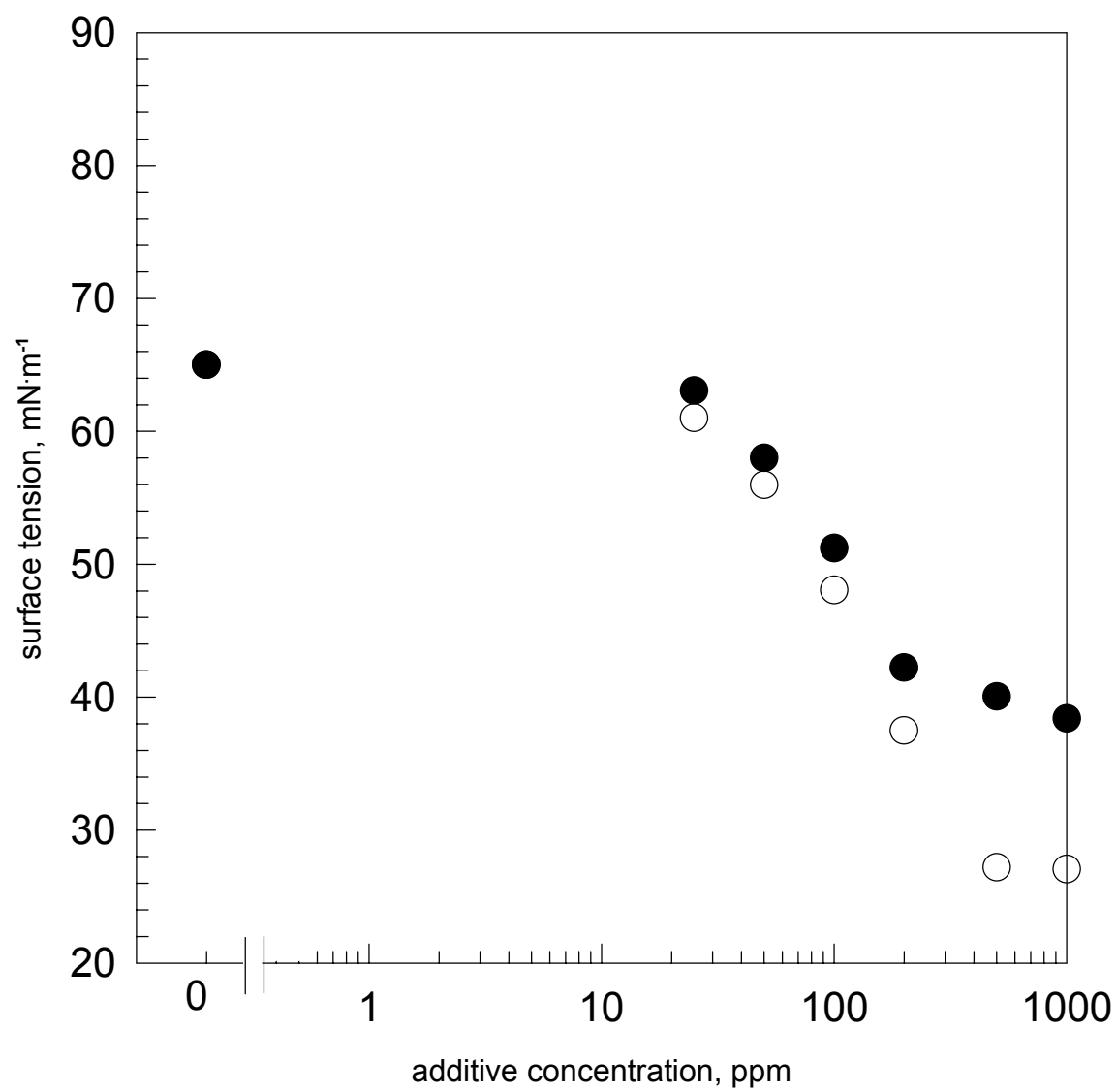


Fig. 6

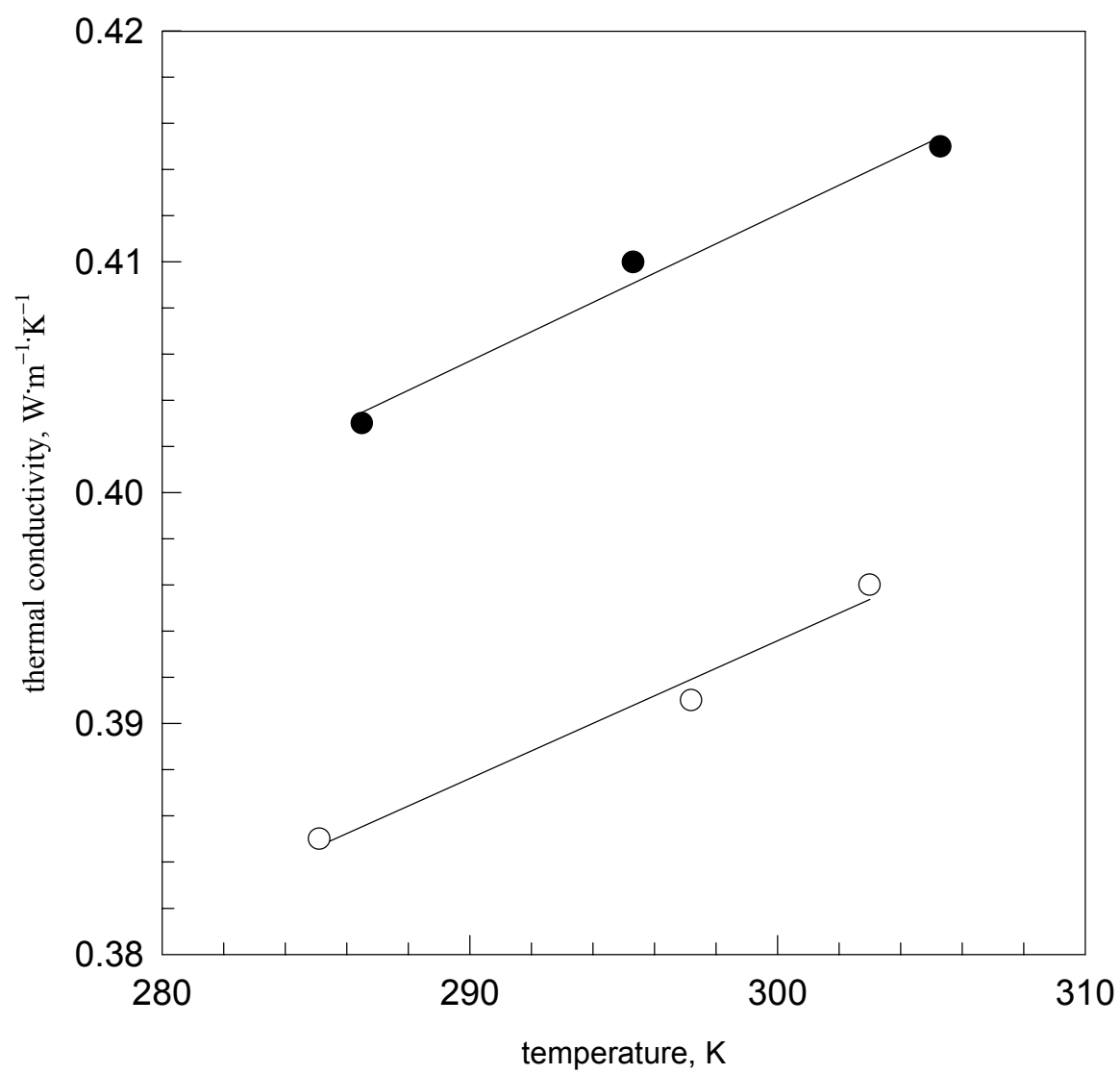


Fig. 7